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14. ABSTRACT This proposal seeks to prepare improved chemical vapor deposition (CVD) and atomic layer deposition (ALD) precursors to materials that contain Sr, Ba, and Ti and ALD precursors for the mid-valent oxides MO (M = Mo, W), M ₂ O ₃ (M = Nb, Ta, Mo, W), and MO ₂ (M = Nb, Ta, Mo, W). These new precursors will be evaluated in film growth trials of MTiO ₃ (M = Sr, Ba) and mid-valent metal oxide films. Specific objectives include the synthesis and characterization of Sr, Ba, and Ti precursors containing bis(pyrazolyl)methane-derived ligands and Nb(III), Ta(III), Nb(IV), Ta(IV), Mo(IV), W(IV), Mo(V), and W(V) precursors with amide-derived ligands.					
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Report Title

New Chemical Precursors for the Growth of Ferroelectric and Mid-Valent Metal Oxide Films

ABSTRACT

This proposal seeks to prepare improved chemical vapor deposition (CVD) and atomic layer deposition (ALD) precursors to materials that contain Sr, Ba, and Ti and ALD precursors for the mid-valent oxides MO (M = Mo, W), M₂O₃ (M = Nb, Ta, Mo, W), and MO₂ (M = Nb, Ta, Mo, W). These new precursors will be evaluated in film growth trials of MTiO₃ (M = Sr, Ba) and mid-valent metal oxide films. Specific objectives include the synthesis and characterization of Sr, Ba, and Ti precursors containing bis(pyrazolyl)methane-derived ligands and Nb(III), Ta(III), Nb(IV), Ta(IV), Mo(II), W(II), Mo(III), W(III), Mo(IV), and W(IV) precursors with amidate-derived ligands, and ALD growth studies of SrTiO₃, BaTiO₃, MO, M₂O₃, and MO₂ films using the new precursors. Successful execution of the proposed work would afford optimized CVD and ALD precursors for Sr, Ba, and Ti, demonstration of the ALD growth of crystalline MTiO₃ films from these precursors, new precursors for mid-valent oxides of Nb, Ta, Mo, and W, and demonstration of the ALD growth of these oxides. This work would broadly impact research in ferroelectric materials containing based upon SrTiO₃ and BaTiO₃ and could lead to breakthroughs in the development of resistive memory devices.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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(b) Papers published in non-peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

02/20/2014 1.00 Charles H. Winter, Thomas J. Knisley, Lakmal C. Kalutarage, Mark A. Zavada, Joseph P. Klesko, T. Hiran Perera. Metallic Materials Deposition: Metal-Organic Precursors, Encyclopedia of Inorganic and Bioinorganic Chemistry (05 2012)

TOTAL: 1

Number of Manuscripts:

BooksReceivedPaper**TOTAL:**

Patents Submitted

Patents Awarded

Awards

Editorial Advisory Board, Organometallics, 2012-2014
Conference Chair, 2015 AVS International ALD Meeting

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Mark A. Zavada	1.00	
T. Hiran Perera	0.10	
FTE Equivalent:	1.10	
Total Number:	2	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Charles H. Winter	0.10	
FTE Equivalent:	0.10	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Michael K. Schlager	0.23	Chemistry
Joseph Baumann	0.23	Chemistry
FTE Equivalent:	0.46	
Total Number:	2	

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Names of Personnel receiving masters degrees

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Total Number:

Names of personnel receiving PHDs

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T. Hiran Perera

Total Number:

1

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

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Technology Transfer

1. Foreword

This project sought to prepare improved chemical vapor deposition (CVD) and atomic layer deposition (ALD) film growth precursors for various materials that contain the heavier group 2 elements Sr and Ba. Another goal was to prepare ALD precursors for mid-valent oxides such as MO (M = Mo, W), M₂O₃ (M = Nb, Ta, Mo, W), and MO₂ (M = Nb, Ta, Mo, W). Selected precursors were evaluated in thin film growth trials to assess and demonstrate their viability in the growth of mid-valent metal oxide films. Thin films of the materials proposed herein encompass a broad range of military and civilian applications, as noted below. As a central research goal, we sought to develop chemical insight into precursor structures that combine high thermal stability and maximum volatility, while also matching the growth chemistry of the precursor to that of the desired material. CVD and ALD precursors for Sr and Ba remain problematic due to the low vapor pressures associated with oligomeric structures, low thermal stabilities, and erratic vapor transport. Mid-valent oxides of the group 4-6 metals are emerging as critical low resistivity materials in resistive random access memory (ReRAM) devices that are based upon metal/metal oxide/metal architectures, but thin films of these mid-valent oxides remain scarcely documented.

2. Statement of the problem studied

Project Summary: This proposal seeks to prepare improved chemical vapor deposition (CVD) and atomic layer deposition (ALD) precursors to materials that contain Sr, Ba, and Ti and ALD precursors for the mid-valent oxides MO (M = Mo, W), M₂O₃ (M = Nb, Ta, Mo, W), and MO₂ (M = Nb, Ta, Mo, W). These new precursors will be evaluated in film growth trials of MTiO₃ (M = Sr, Ba) and mid-valent metal oxide films. Specific objectives include the synthesis and characterization of Sr, Ba, and Ti precursors containing bis(pyrazolyl)methane-derived ligands and Nb(III), Ta(III), Nb(IV), Ta(IV), Mo(II), W(II), Mo(III), W(III), Mo(IV), and W(IV) precursors with amidate-derived ligands, and ALD growth studies of SrTiO₃, BaTiO₃, MO, M₂O₃, and MO₂ films using the new precursors. Successful execution of the proposed work would afford optimized CVD and ALD precursors for Sr, Ba, and Ti, demonstration of the ALD growth of crystalline MTiO₃ films from these precursors, new precursors for mid-valent oxides of Nb, Ta, Mo, and W, and demonstration of the ALD growth of these oxides. This work would broadly impact research in ferroelectric materials containing based upon SrTiO₃ and BaTiO₃ and could lead to breakthroughs in the development of resistive memory devices.

3. Summary of the most important results

Metal Complexes Containing Bis(pyrazolyl)carboxylate Ligands. In our previous ARO-supported grant, we reported the synthesis, structure, volatility, and thermal stability of a series of Ca, Sr, and Ba complexes that contain tris(pyrazolyl)borate ligands.¹ Significantly, these complexes are highly stable thermally, sublime without decomposition, and are thus potentially useful ALD and CVD precursors for SrTiO₃ and BaTiO₃ films. However, subsequent ALD studies with water as the oxygen source revealed that MB₂O₄ films resulted, demonstrating that B from the ligands is efficiently incorporated into the films.² Work in the present project was motivated by the goal of eliminating B from the ligands, while still retaining the volatility and high thermal stability of the tris(pyrazolyl)borate complexes. We hypothesized that B-free bis(pyrazolyl)carboxylate ligands might afford useful Ca, Sr, and Ba precursors, and a goal of the project was to assess this possibility. Since Ca, Sr, and Ba coordination chemistry can be complicated, we initially sought to prepare first row transition metal(II) complexes containing bis(pyrazolyl)carboxylate ligands, since the latter should be easier to prepare. If these complexes

showed good precursor properties, then it is likely that the Ca, Sr, and Ba complexes would also be useful precursors. As outlined in Scheme 1, we prepared the Cu, Ni, Co, Fe, Mn, and Zn complexes **1-15**, which contain various substituted bis(pyrazolyl)carboxylate ligands. These complexes were isolated in 60-80% yields as crystalline solids. X-ray crystal structures of **1-15** were determined to establish their solid state geometries. Figure 1 shows representative perspective views of **6** and **10**. All complexes showed similar 6-coordinate geometries. Sublimation studies of **1-15** revealed that all of these complexes decompose in the solid state between 175-185 °C at 0.05 Torr without subliming. Hence, none of these complexes is volatile. A careful examination of the thermogravimetric analysis traces revealed that the initial decomposition event appears to correspond to loss of CO₂, which then leads to decomposition and non-volatile residues. Bis(pyrazolyl)methyl anions are stabilized due to conjugation with the pyrazolyl π -systems, so a relatively low decarboxylation temperature ensues.

Scheme 1. Synthesis of Complexes **1-15**.

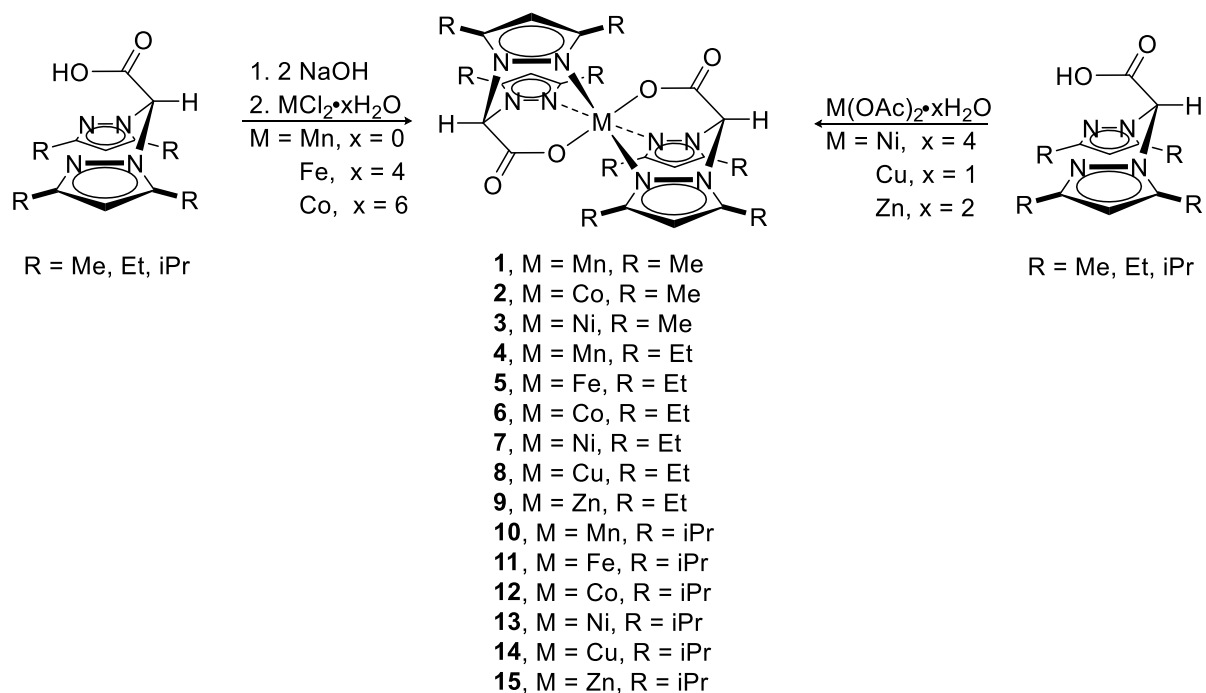
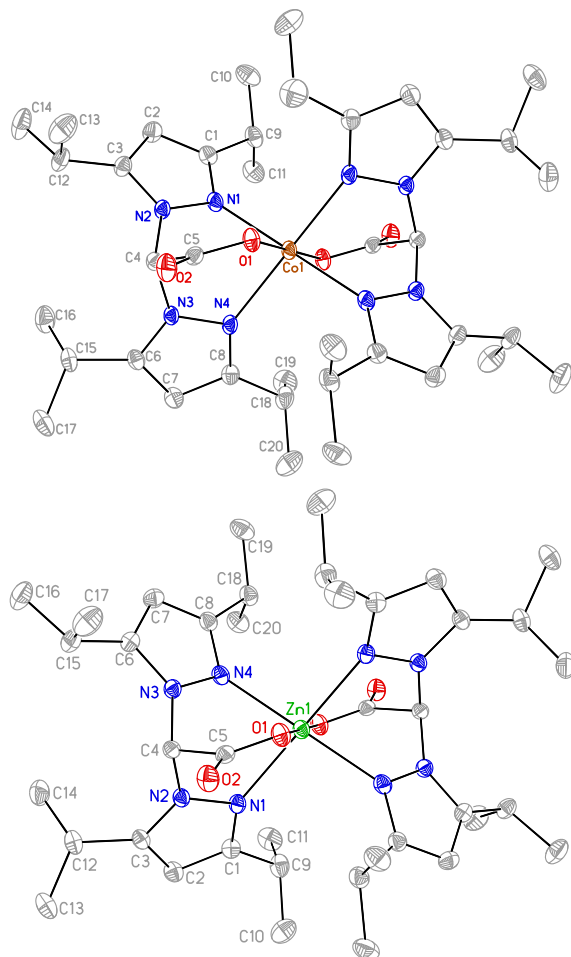
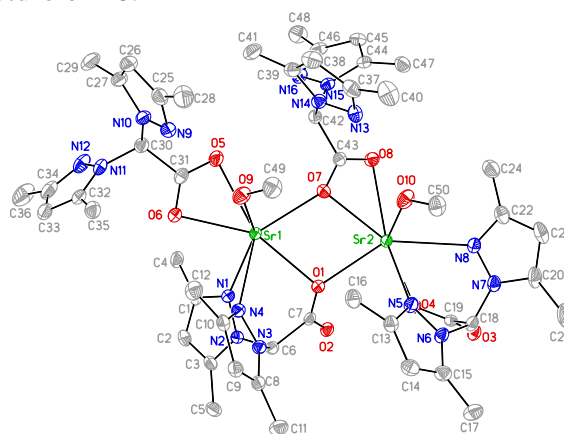


Figure 1. Molecular Structures of **6** (top) and **10** (bottom) Determined by X-Ray Crystallography.



Numerous reactions were carried out in attempts to synthesize Ca, Sr, and Ba analogs of **1-15**. In one successful reaction, the dimeric Sr complex $\text{Sr}_2((\text{Me}_2\text{pyrazolyl})_2\text{CHCO}_2)_4(\text{MeOH})_2$ (**16**) was crystallized from methanol and its X-ray crystal structure was determined. As shown in Figure 2, this complex exists as a dimer in the solid state, with one terminal bis(pyrazolyl)carboxylate ligand per Sr ion, and two bridging bis(pyrazolyl)carboxylate ligands between the Sr ions. Each Sr ion crystallizes with a methanol ligand. Attempts to sublime **16** led to solid state decomposition at about 180 °C, which appears to occur via loss of CO_2 .

Figure 2. Molecular Structure of **16**.



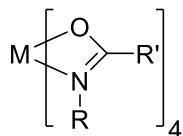
Complexes **1-16** were synthesized and characterized, but they are not volatile and thus are not useful precursors for CVD and ALD. The decompositions occur by loss of CO₂ from the ligands, which leads to decomposition. We are preparing a manuscript that describes the synthesis, structure, and properties of **1-15** (Zavada, M.A.; Heeg, M.J.; Martin, P.D.; Winter, C.H., in progress).

The student who was supported on this grant during 2012-2013, Mark A. Zavada, quit the Ph.D. program in his third year to take a job at a local chemical company. His resignation was on 3/31/13, which was part way through the one year period of this grant. Needless to say, his departure was devastating for this project. Undergraduate students Michael K. Schlagel (chemistry major from Bowdoin College) and Joseph Baumann (chemistry major from Grand Valley State University) were hired during the summer of 2013 to help clean up the syntheses of **1-16**. Mr. Schlagel is currently a junior chemistry major at Bowdoin College, and is likely to work in the PI's laboratory during the summer of 2014. Mr. Baumann joined the Wayne State University Ph.D. program starting in the Fall of 2013, and is currently working in the PI's laboratory on ALD film growth.

Synthesis of Precursors to MO₂ Films. We sought to prepare Nb(IV) and Ta(IV) complexes that are thermally stable and volatile, and which might serve as precursors for the ALD growth of MO₂ films. We have previously demonstrated the ALD growth of W₂O₃ films using the dimeric W(III) precursor W₂(NMe₂)₆ and water.³ We have discovered that amidate ligands are highly resistant to metal insertion decomposition pathways in Nb(IV) and Ta(IV) and also afford complexes with potentially useful ALD precursor properties. Amidate ligands are obtained upon deprotonation of organic amides RNHCOR', and bind to metal ions with a κ^2 -N,O-bonding motif. Organic amides are easily prepared with a large range of R and R' groups, which permits facile fine-tuning of the precursor properties.

Nb(IV) and Ta(IV) complexes **17** and **18** were synthesized in 55-83% yields upon treatment of NbCl₄(THF)₂ or TaCl₄(py)₂ with 4 equivalents of the lithium amidate salts as deep maroon (**17**) or purple (**18**) crystalline solids, and X-ray crystal structures demonstrated monomeric species with dodecahedral geometry about the metal ions. Table 1 gives some precursor properties for selected examples of **17**. These complexes sublime on 0.5-1.0 gram scales in 2-3 hours between 110 and 145 °C with < 2% nonvolatile residue at the end of the sublimations. Complexes **17a-c** and **17e** undergo solid state decomposition at ~270 °C, as evidenced by a color change from deep maroon to pink. These preliminary studies suggest that

17a, **17b**, **17c**, and **17e** have sufficient volatility and thermal stability to serve as ALD precursors. Complex **17a** is the most promising precursor due to its high volatility. Figure 2 shows a representative X-ray crystal structure of **17a**, which exists as an 8-coordinate monomer. A paper describing the synthesis, structure and properties of **17** and **18** is in progress.



17, M = Nb

17a, R = tBu, R' = Me

17b, R = tBu, R' = Et

17c, R = tBu, R' = iPr

17d, R = tBu, R' = tBu

17e, R = iPr, R' = Et

17f, R = iPr, R' = iPr

17g, R = Et, R' = tBu

18, M = Ta

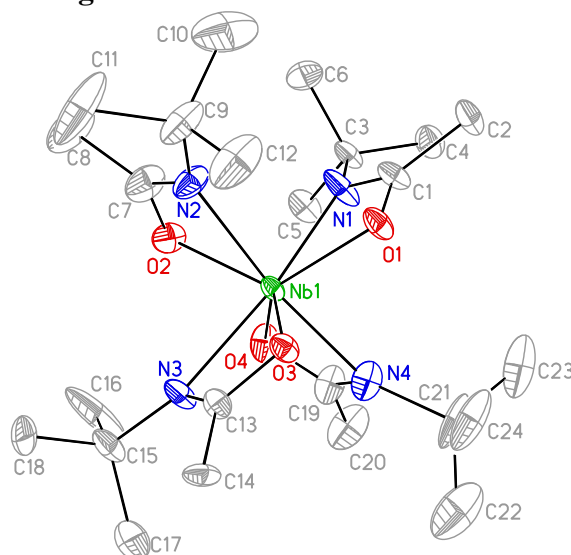
18a, R = tBu, R' = Et

18b, R = tBu, R' = iPr

Table 1. Preliminary precursor properties of **17a**, **17b**, **17c**, and **17e**.

Complex	Mp, °C	Subl. Temp. °C/0.05 Torr	Dec. Temp. °C
17a	177	110-120	~270
17b	158	125-135	~270
17c	>270	140-145	~270
17e	190	135-140	~270

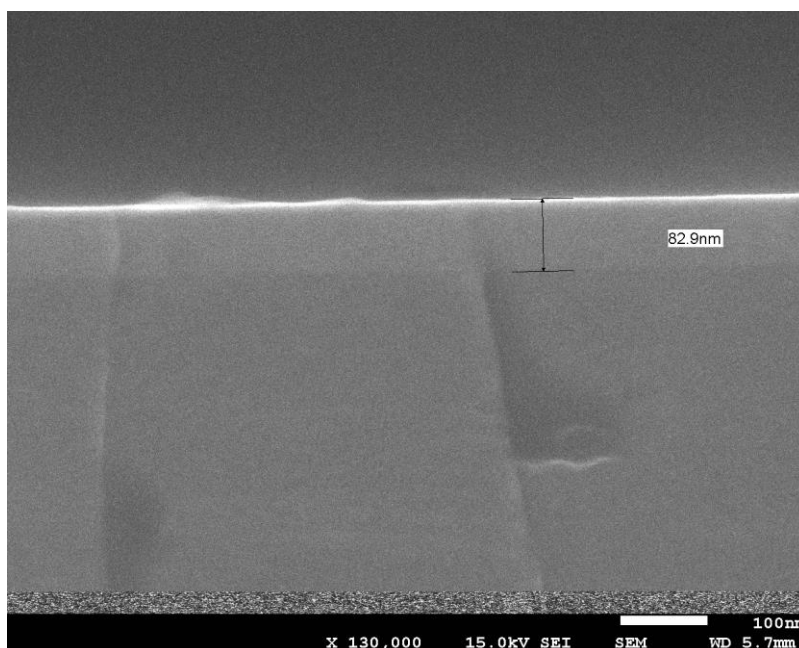
Figure 2. Molecular Structure of **17a**.



Attempted Growth of NbO_x Films Using 10a. One of the goals of this project was to grow films of mid-valent oxides by ALD from appropriate mid-valent precursors. Since **17a** has useful precursor properties, it was prepared on a 10 gram scale and initial ALD growth trials

were carried out. Complex **17a** was delivered at a source temperature of 160 °C in our ALD reactor, and the substrate temperature was 250 °C. With water as the oxygen source, no film growth was observed on Si/SiO₂ substrates under any conditions. Our assessment was that **17a** is not reactive enough toward water to support ALD growth. Accordingly, a deposition with **17a** was repeated at 250 °C, but ozone was used as a more reactive oxygen source. With 2000 growth cycles, an 83 nm thick metallic blue film was obtained on Si/SiO₂, which implies a growth rate of about 0.4 Å/cycle. Figure 3 shows a side-view scanning electron micrograph of an 82.9 nm thick as deposited NbO_x film. The surface is very smooth and the film thickness is very uniform, both of which are characteristics of ALD-grown films. This film was amorphous to X-ray diffraction as-deposited. After annealing at 400 °C for 5 hours under nitrogen, the film still remained amorphous. However, annealing at 600 °C for 5 hours led to the emergence of crystalline Nb₂O₅, JCPDS 32-0710. Precursor **17a** is exceptionally air sensitive, and initial ALD studies suggested that there was an air leak in the ALD reactor. We ended up replacing the low vapor pressure source delivery system in the fall of 2013, which fixed the leak problem. However, it took approximately 4 months to order and receive the new part, which was past the end of the current project. Accordingly, the chemical composition of the as deposited NbO_x film remains uncertain. Conversion of **17a** to a film required ozone as the oxygen source, and it is possible that the ozone oxidized the Nb(IV) center in **17a** to Nb(V), which gave amorphous Nb₂O₅ films that only crystallized upon heating to 600 °C. It is also possible that amorphous NbO₂ films resulted, which either oxidized to Nb₂O₅ upon exposure to ambient atmosphere or were oxidized to Nb₂O₅ by traces of oxygen or water upon annealing at 600 °C.

Figure 3. Scanning Electron Micrograph of a NbO_x Film Growth at 250 °C on Si/SiO₂ with Ozone as the Oxidant.



Review Article. We published a review article on metalorganic film growth precursors that were reported between 2005 and 2012.⁴ This article appeared in “Encyclopedia of Inorganic and Bioinorganic Chemistry” in December 2012.

4. Bibliography

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